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SOME PHYSICAL PROPERTIES OF BUFFALO'S MILK CASEINATE POWDERS.

BY

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ABSTRACT

Buffalo's milk caseinates were obtained under different precipitation conditions and were oven dried (60 °C) or freeze- dried. Dried samples were milled in a Hammer mill and the powders were tested for their sorption isotherms behavior (at water activity range of 0.11 to 0.85 at 30°C), particle size distribution characteristics, bulk density, and tristimulus colour parameters, (lightness, (L), redness (a), yellowness (b), and chroma. Results showed that freeze-dried casein samples achieved higher equilibrium moisture content than oven dried samples at all a_w -values. The monolayer moisture contents (M_0-values) ranged from 0.013 to 0.0593g H_2O/g solids, while the energy constant (C) showed higher values (15.55 - 103.96) for the oven dried samples and lower values (15.44 to 23.49) for the freeze dried samples, which indicate that water molecules were strongly bounded to the oven dried samples. Similarly, surface area of the freeze-dried samples was higher than those of oven-dried samples indicating the compactness of the casein molecule in the oven dried samples. The mean particle size ranged between 0.4904mm for oven dried lactic acid casein and 0.3593 mm for freeze-dried rennet casein. Also, median and modal means as well as specific surface area and fineness modulus and index were given for the casein powders. Bulk density of casein powders were increased by increasing particle size and the rate of increase was more remarkable for groups of particle size higher than 0.25 mm. Total milk proteinate and rennet casein powders (oven or freeze-dried) showed higher bulk density values than those of lactic acid casein. Colour parameters of the caseinate powders were affected by the applied preparation and drying methods. Freeze-dried samples were characterized by higher L and lower b values than those of oven dried samples. The lightness (L-values) were decreased while redness (a-values) and yellowness (b-values) were increased during storage of caseinate powder at different water activity values (from 0.11 to 0.85).

Key words: Buffalo's milk caseinates, Sorption isotherms, Particle size distribution, Bulk density, Chroma, Surface area, Energy constant.

INTRODUCTION

Caseinates obtained from buffalo's milk are essential ingredients for many food industries including ice cream mixes, dairy products as well as sausage, bread and meat products. Because of their numerous functional

properties such as bulking and water binding, their use has been widely spread. The functional properties of caseinate powders depend on their particulate characteristics such as bulk density, particle sizes, as well as colour and moisture content. The knowledge of moisture sorption isotherms of dehydrated food items is valuable in solving food processing and engineering problems such as equipment design, drying and storage processes as well as prediction of shelf-life. The storage, handling and processing of food materials may induce a complicated stress pattern due to material expansion and contraction (Rao, 1975). The ability of biological materials to resist such stress cracks depends upon material properties, mechanical and physical as well as on the environmental condition during storage and processing. Mann and Malik, (1996) found that buffalo's milk whey protein concentrate differs in the sorption properties depending on the method used for precipitation. On the other side, Foster *et. al.*, (2005) showed that the sorption isotherms characteristics of whey and casein powders were not temperature dependent over the temperature range of 4 –37 °C. Storage of milk powders under adverse conditions accelerates the normally slow deter- ioration in nutritional quality (Ford *et al.*, 1983). The particle size specifications of ground material and powder is a very important physical characteristic affects storage stability and solubility. The purpose of grinding and size reduction of dried materials is the enlargement of surface area through creation of new surfaces. Therefore, the specific surface area is a measure for the efficiency of the grinding process and for the functionality of the obtained powder. Recent studies on particle sizes distribution of dried milk and whey products (Gursoy, *et al.*, 2001, Keogh *et al.*, 2002, Keogh *et al.*, 2004 and Banavara *et al.*, 2003) revealed that particle size and particle size distribution affecting properties and functionality of spray dried milk powder, as well as commercial sweet whey powders. Bulk (or apparent) density is the mass of particles that occupies a unit volume of the bed. It is an important physical properties which affect handling, packaging, storage and porosity of powders. Harish and Baht, (2004) found that modified milk powder showed increase dispersebility and decrease in solubility and bulk density. On the other side, Yetismeyen and Deveci (2000) as well as Shakeel–Ur-Rehman *et al.*, (2003) found that packaging material and storage influence the bulk density of milk powders and induce some morphological changes in particle shape and structure. Colour of milk powders is an important quality. Lactose and sugar content can affect colour characteristics of milk powders during processing and storage. Studies on sweet whey powder (Ford *et al.*, 1983, Burin *et al.*, 2001 as well as Sithole *et al.*, 2005) reveald that there was a comparison between the rate of Millard browning and the change in colour measured by Hunter method. They found that Hunter L and a values appeared most sensitive to change during storage.

Studies on the physical properties of buffalo's milk caseinate powders are scarce. Therefore, the objective of the present work was to shed some lights on the sorption isotherms, particle size distribution, bulk density and colour parameters of buffalo's milk caseinate powders.

MATERIALS AND METHODS

Materials:

Raw buffalo's milk was obtained from the herd of the Faculty of Agriculture, Ain Shams University, Cairo, Egypt.

Preparation of milk protein products:

Total milk proteinate, lactic acid casein and rennet casein were prepared according to the method described by Morr (1985). Total milk proteinate was prepared as follows: 10 kilograms of buffalo's skim milk were alkalined by 1 N NaOH to pH 10 and heated to 50 °C±1 to solubilize casein micelles. After that, pH was then adjusted to 3.5 at 40 °C to complex the whey protein and casein using 1 N HCl. Again the pH was raised to 4.6 by 1 N NaOH to precipitate the complexed protein. Coagulated proteins were removed from whey by using cheese cloth. The curd was washed three times (with equal volumes of original milk) by distilled water of 37 - 40 °C, and pH 4.6. The curd was pressed after the final wash and suspended in distilled water by addition of 1N NaOH to bring the pH to 7.5. Rennet casein was prepared by adding 1ml of standard rennet solution per 1kg of skim milk at 37°C. After complete coagulation, cutting and whey drainage, the curd was treated as previously mentioned for total milk proteinate using distilled water. For preparation of lactic acid casein, raw skim milk was coagulated at pH 4.6 using lactic acid 2 N at 37 °C and the curd was treated as previously mentioned for total milk protein. Prepared protein samples were divided each in two portions. One portion was dried in oven at 60 °C for 6 hr, while the second portion was lyophilized at -40 °C by freeze drying system LYPH-LOCK-4.5. The moisture content of the dried samples ranged from 2 to 10%, while the protein content was in the range of 88 to 91%.

Milling of samples:

The investigated dried samples (total milk proteinate, lactic acid casein and rennet casein) were prepared in a powder form by milling in a laboratory type hammer mill (DCFH 48 Germany).

Equilibrium moisture content and water activity:

Equilibrium moisture experiments were carried out by applying the gravimetric method as described by Kameoka *et al.*, (1985). Saturated salt solutions were used to control the humidity (water activity a_w) at the constant temperatures. Eight humidity control desiccators, for each desired relative humidity, were placed at room temperature. About 2 g of protein samples were placed into separate petri glass dishes and then these six samples holders were put in the same humidity desiccator. The change in weight was recorded, after interval of 2-5days, till no further change in weight was observed and percentage of moisture content on dry weight basis (g H_2O/ 100g solids) was calculated. Sorption isotherms curves were plotted by taking 0.11 to 0.85 a_w on x- axis and the corresponding equilibrium moisture content of the casein samples on y- axis. Equilibrium moisture contents of the casein samples were achieved in a period of 21-30 days.

Particle size distribution:

A weight of 100g casein powder sample was placed at the top surface of a graded set of sieves of 0.7, 0.5, 0.315, 0.25, 0.20 and 0.10 mm. The stack of sieves with the attached collecting pan was mechanically shaken by vibrator (MLW Labortechnik, Ilmenau, Germany) at speed (8) until the weight of the material on the smallest screen (0.1mm) had reached equilibrium. When sieving was completed, the residual material on each sieve was weighed. The aforementioned procedure was adapted from Phillips *et al.*, (1988). The particle size distribution was evaluated according to the following parameters (Henderson and Perry, 1976 as well as Stiess, 1995):

A) **Mean particle size** (Xr in mm), which is the summation value resulting from the product of **individual particle sizes** (Xi) multiplied by its corresponding mass fraction (**ΔD**):

$$Xr = Xi \,.\, \Delta D \qquad (1)$$

Standard deviation (S) around the mean value (Xr) was calculated as follows:

$$S = \sqrt{(X_i - X_r)^2 / (n-1)} \qquad (2)$$

Where n = Number of sieves

B) **Median value** (X_{50}): which is the particle size, under which lie 50% of the sample mass. It is the cross point of the accumulative mass distribution curve with the 50% horizontal line.

C) **Modal value** (X_h): which is the richest particle size group and could be obtained from the maximum of the distribution density

$$q = \Delta D / \Delta X \qquad (3)$$

Where ΔX is the distance (difference) between the pore size of two successive sieves.

D) **Specific surface area** (Sv), which represent the surface area of a volume unit

$$(mm^2/mm^3)\ Sv = 6\, f \sum_{i=1}^{n} \Delta D / \bar{x} \qquad (4)$$

Where f is a shape correction factor (For sphere f =1 and for broken shapes f = (1.2 –1.5).

E) **Sauter diameter** (d_{32}): it is the diameter of a sphere representing the entire particle collective (groups) of the tested powder and could be calculated as follows:

$$d_{32} = 6 / Sv \ (mm) \qquad (5)$$

F) **Fineness modulus:** is the sum of the weight fraction (ΔD) retained above each sieve multiplied by the sieve number (Nr.) in the used sieve set, divided by 100. It gives more relationship of the proportion of coarse, medium and fine materials.

G) **Uniformity index:** It indicates the amount of coarse, medium and fine materials in the powder sample, which are not indicated by the fineness modulus.

Bulk density determination:

Bulk density was determined according to Bencini (1986) by pouring 20 g of specific meshing measurements of the samples (0.20, 0.25, 0.315 and 0.50 mm) in 50 ml graduated cylinders. The bulk density was calculated after

orientation and re-arrangement of the tested samples by knocking 10 times over the bench table. The values are the average of three replicates and given as g (actual weight)/ml.

Colour measurements:

Colour parameters of the casein powders were determined according to the tristimulus Colour system described by Francis, (1983) using spectrophotometer (**MOM, 100 D, Hungary**). Colour coordinates **X, Y,** and **Z** were converted to corresponding Hunter **L, a, b** colour coordinates according to formulas given by manufacturer. **L** indicates lightness or darkness in a scale from 100.0 to 0.0, while **a** and **b** represent the coordinates of (red – green and yellow – blue) on a scale from plus 60 to minus 60. Hue angle, which represents the dominating colour, was calculated as follows:

$$\text{Hue} = \tan^{-1} b/a \qquad (6)$$

The colour intensity (chroma) and total colour index (**ΔE ab**) were calculated as follows:

$$(\Delta E\ ab) = (a^2 + b^2 + L^2)^{1/2}\ C = (a^2 + b^2)^{1/2} \qquad (7)$$

RESULTS AND DISCUSSION

Sorption isotherms of caseinate powders:

Data in Table (1) show the equilibrium moisture content (g H_2O/100g solids) of the obtained casein powders at different water activity values, ranging from a_w 0.11 to a_w 0.85. The relationship between water activity and equilibrium moisture content values were plotted in form of sorption isotherms curves as given in Fig. (1 a, b, and c). As seen, equilibrium moisture content values were increased by increasing water activity values. The increase in moisture content could be divided into three regions as follows. Region one starts from a_w - 0.11 to a_w - 0.33 and is characterized by a rapid increase in the equilibrium moisture content of the dried samples. In the second region (from a_w - 0.33 to a_w - 0.66) the equilibrium moisture content remains more or less constant and then there is an abward change in the isotherm curve. The maximum equilibrium moisture content achieved at a_w - 0.85 ranged between 10.46 to 19.00 g H_2O/100g solids. Differences were found to depend on the type of the casein and method of drying. At a_w - 0.85, oven dried total milk proteinate reached moisture content of 15.58, while that of oven dried lactic acid casein reached only 10.46 g H_2O/100g solids. Freeze-dried casein samples achieved higher moisture content than oven dried samples. The shape of sorption isotherm curves could be generally characterized as a typical Segmoidal type. Drops in the sorption isotherm curve at a_w values between 0.33 and 0.55 could be referred, as reported by Mann and Malik (1996), to some phase changes in protein fractions and lactose crystallite. The maximum moisture content of the casein preparates obtained in the present work were lower than those reported by Mann and Malik (1996) for whey protein concentrates, may be due to the difference in their sugar contents. It is of interest to apply BET (Brunauer- Emmnett -Teller) equation to describe the equilibrium isotherms of dried food as follows, (Heldman and Singh 1981):

Table (1): Equilibrium moisture content (g H_2O/100g solids) of buffalo's milk caseinate powder at different water activity values (30 °C).

Water activity a_w	Equilibrium moisture content (g H_2O/100g solids).					
	Total milk proteinate		Lactic acid casein		Rennet casein	
	Oven dried	Freeze dried	Oven dried	Freeze dried	Oven dried	Freeze dried
0.11	4.68	5.962	2.05	9.06	4.476	6.636
0.22	7.10	7.110	3.757	9.725	4.896	7.876
0.33	10.46	12.77	7.164	15.388	11.03	14.2378
0.44	9.11	10.113	7.802	15.277	9. 09	13.586
0.55	11.20	10.778	6.73	14.22	8.99	11.704
0.66	13.00	11.440	7.02	15.055	9.406	12.645
0.75	13.368	12.72	9.789	15.55	11.557	14.383
0.85	15.58	15.44	10.64	19.00	12.76	16.916

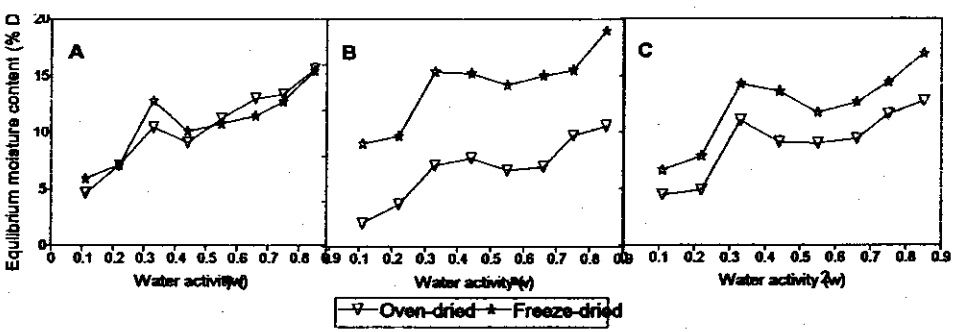

Fig. (1): Sorption isotherms curves of buffalo's milk caseinate powders: (A) Total milk proteinate, (B) Lactic acid casein, (C) Rennet casein.

$$a_w/M(1-a_w) = 1/M_0 C + (C-1/M_0 C) \cdot a_w \quad (8)$$

Where: a_w is the water activity, M: is the corresponding moisture content, M_0 is a monolayer moisture content which gives the number of water molecule required to cover the surface of the casein with a layer of one molecule thickness, and C is an energy constant indicative of the nature of sorption. The M_0 value is directly related to the surface area (A) of the sorptive sites and could be calculated using the following: equation (Mann and Malik 1996):

$$A = M_0 * N * A_{H2O} / M_{H2O} \quad (9)$$

Where: M_{H2O}: weight of water molecule, A_{H2O}: Surface area of a water molecule (10.8 $Å^2$), N: is Avogadro number ($6 \cdot 10^{23}$) molecules/mol. Table (2) shows the values of M_0, C and A for the tested casein samples. As seen, M_0 (g H_2O/g solids) were relatively low (0.013 to 0.0514) for oven dried casein samples and relatively high for those freeze dried (0.0472 to 0.0593), which indicate that the freeze-dried samples were more porous than those oven dried samples. On the same time, the energy constant (C) showed higher values (15.55 – 103.96) for the oven dried samples and lower values from 15.44 to 23.49 for the freeze dried samples, which indicate that water molecules were strongly bounded in the oven

dried samples. Similarly, surface area of the freeze-dried samples was higher than those oven-dried samples indicating the compactness of the casein molecule in the oven dried samples. The obtained results agree with those reported by Mann and Malik (1996) and indicate that powdered buffalo's casein could be safetly stored at 55% relative humidity and 30 °C.

Table (2): Moisture sorption parameters of casein powders obtained from buffalo's milk.

Casein powder type	Monolayer moisture (M_0) gH_2o/g solids	Energy constant (C)	Surface area of protein (m^2/g solids)
Total milk proteinate			
Oven -dried	0.0514	103.96	1713.20
Freeze-dried	0.0472	23.49	1573.35
Lactic acid casein			
Oven -dried	0.0384	15.55	1277.34
Freeze-dried	0.0593	15.44	1977.30
Rennet casein			
Oven -dried	0.0130	70.70	431.66
Freeze-dried	0.0544	23.44	1813.32

Particle size:

Data of Particle size analysis of the tested casein powders are given in Table (3) and graphically presented in Fig.(2). The table includes parameters of the sieve system characteristics as well as some parameters of the tested caseinate powder samples. The sieve system characteristics includes sieve size (X) in mm, distance in pore size of two successive sieves (ΔX in mm) as well as the mean sieve size ($\bar{X}$ in mm). The powder characteristics include the mass fraction (ΔD) remained on each sieve, the accumulative mass passage in percent (Dj), the distribution density (q) representing $\Delta D/ \Delta X$, the mean particle size of each collected fraction ($\bar{X}*\Delta D$) as well as the surface area of each collected fraction. These data were calculated for oven and freeze-dried total milk proteinate, lactic acid casein and rennet casein. Data given in Table (3) were used to calculate the different particle mean size parameters (X_r, X_{50}, X_h, S_v, Sauter diameter, fineness modulus and uniformity index) as explained before. The calculated parameters are given in Table (4). As seen, the mean particle size X_r was the maximum (0.4904 mm) for oven dried lactic acid casein and the minimum (0.3593 mm) for freeze dried rennet casein. However, the mean particle size (X_r) values were characterized by a very wide scattering around the mean value, since the standard deviation values (S values) were relatively high ranging from ± 0.297 to ± 0.1599. Generally, the X_r - values were relatively higher than the 0.183 mm reported for whey powders (Banavara *et al.*, 2003). The reason could be referred to the type of milling equipment, since the Hammer mill gives a high percent of coarse particles because a considerable portion of input energy was lost in heat generation instead of being used in particle disintegration (Hall, 1972). The Median value (X_{50}) of the tested casein samples show lower values than (X_r) for the freeze-dried samples and higher or similar values for the oven dried samples.

Table (3a) Sieve analysis results of buffalo's milk cascinate powders (Total milk proreinate).

Nr. of sieve in sieve set	Sieve system characteristics			Particle parameters of total milk proteinate										
				Oven-dried total milk proteinate					Freeze-dried total milk proteinate					
	Sieve size x(mm)	Bore distance Δ x (mm)	Mean sieve size $\bar{X}$ (mm)	Mass fraction ΔD= Δ m/m	Acumulativ mass passage Dj %	Distribution density q= Δ D/ Δ x	Fraction mean particle $\bar{X}$. Δ D	Fraction surface area Δ D/$\bar{x}$	Mass fraction ΔD= Δ m/m	Acumulativ mass passage Dj %	Distribution density q= Δ D/ Δ x	Fraction mean particle $\bar{X}$. Δ D	Fraction surface area Δ D/$\bar{x}$
Pan	0												
6	0.1	0.1	0.05	0.0027	0.27	0.027	0.00013	0.054	0.0038	0.38	0.038	1.9×10^{-4}	0.076
5	0.2	0.1	0.15	0.0427	4.54	0.427	0.00641	0.2846	0.0956	9.94	0.956	0.01434	0.6373
4	0.25	0.05	0.225	0.0429	8.83	0.858	0.00965	0.1906	0.0808	18.02	1.616	0.01818	0.3591
3	0.315	0.065	0.283	0.2504	33.87	3.852	0.0709	0.8848	0.1436	32.65	2.209	0.04064	0.5074
2	0.50	0.185	0.407	0.3344	67.31	1.808	0.1361	0.8216	0.3474	67.39	1.8778	0.14139	0.85356
1	0.70	0.20	0.60	0.3149	99.8	1.575	0.1889	0.5248	0.3141	99.98	1.5705	0.18846	0.5235
							Σ=0.412 mm	Σ= 2.76 mm^{-1}				Σ=0.4057 mm	Σ=2.957 mm^{-1}

Table (3b) Sieve analysis results of buffalo's milk caseinate powders (Lactic acid casein).

Nr. of sieve in sieve set	Sieve system characteristics			Particle parameters of lactic acid casein									
				Oven-dried lactic acid casein					Freeze-dried lactic acid casein				
	Sieve size x(mm)	Bore distance Δx (mm)	Mean sieve size $\bar{X}$ (mm)	Mass fraction $\Delta D = \Delta m/m$	Acumulativ mass passage Dj %	Distribution density $q = \Delta D/\Delta x$	Fraction mean particle $\bar{X} \cdot \Delta D$	Fraction surface area $\Delta D/\bar{x}$	Mass fraction $\Delta D = \Delta m/m$	Acumulativ mass passage Dj %	Distribution density $q = \Delta D/\Delta x$	Fraction mean particle $\bar{X} \cdot \Delta D$	Fraction surface area $\Delta D/\bar{x}$
Pan	0												
6	0.1	0.1	0.05	0.0016	0.16	0.016	$8x10^{-5}$	0.032	0.0006	0.06	0.006	$3x10^{-5}$	0.012
5	0.2	0.1	0.15	0.0300	3.16	0.30	0.0045	0.200	0.0257	2.63	0.257	0.00385	0.1713
4	0.25	0.05	0.225	0.0416	7.32	0.832	0.00936	0.1849	0.1470	17.33	2.94	0.0331	0.6533
3	0.315	0.065	0.283	0.1062	17.94	1.6338	0.0300	0.3753	0.334	50.72	5.1385	0.0945	1.1802
2	0.50	0.185	0.407	0.20	3 7.95	1.081	0.0814	0.4914	0.2667	77.39	1.4416	0.10855	0.6553
1	0.70	0.20	0.60	0.6085	99.8	3.0425	0.3651	1.0142	0.224	99.98	0.8928	0.1344	0.3733
							Σ=0.490 mm	Σ= 2.298 mm^{-1}				Σ=0.3744 mm	Σ=3.0454 mm^{-1}

Table (3c) Sieve analysis results of buffalo's milk caseinate powders (Rennet casein).

Nr. of sieve in sieve set	Sieve system characteristics			Particle parameters of rennet casein									
				Oven- dried rennet casein					Freeze-dried rennet casein				
	Sieve size x(mm)	Bore distance Δx (mm)	Mean sieve size $\bar{X}$ (mm)	Mass fraction $\Delta D = \Delta m/m$	Acumulativ mass passage Dj %	Distribution density $q = \Delta D/\Delta x$	Fraction mean particle $\bar{X} \cdot \Delta D$	Fraction surface area $\Delta D/\bar{x}$	Mass fraction $\Delta D = \Delta m/m$	Acumulativ mass passage Dj %	Distribution density $q = \Delta D/\Delta x$	Fraction mean particle $\bar{X} \cdot \Delta D$	Fraction surface area $\Delta D/\bar{x}$
Pan	0												
6	0.1	0 . 1	0.05	0.0027	0.27	0.027	1.35×10^{-4}	0.054	0.003	0.30	0.03	1.5×10^{-4}	0.06
5	0.2	0 . 1	0.15	0.0579	6.06	0.579	0.008685	0.386	0.0564	5.94	0.564	0.0084	0.376
4	0.25	0.05	0.225	0.0347	9.53	0.694	0.00781	0.1542	0.0912	15.06	1.824	0.0205	0.4053
3	0.315	0.065	0.283	0.1153	21.06	1.7738	0.0326	0.4074	0.4168	56.74	6.412	0.1179	1.4728
2	0.50	0.185	0.407	0.2416	45.22	1.3059	0.0983	0.5936	0.2391	80.65	1.292	0.0973	0.58747
1	0.70	0.20	0.60	0.5458	99.80	2.729	0.3275	0.9097	0.1915	99.80	0.9575	0.1149	0.31917
							$\Sigma = 0.475$ m m .	$\Sigma = 2.505$ $m m^{-1}$				$\Sigma = 0.3593$ m m .	$\Sigma = 3.221$ mm^{-1}

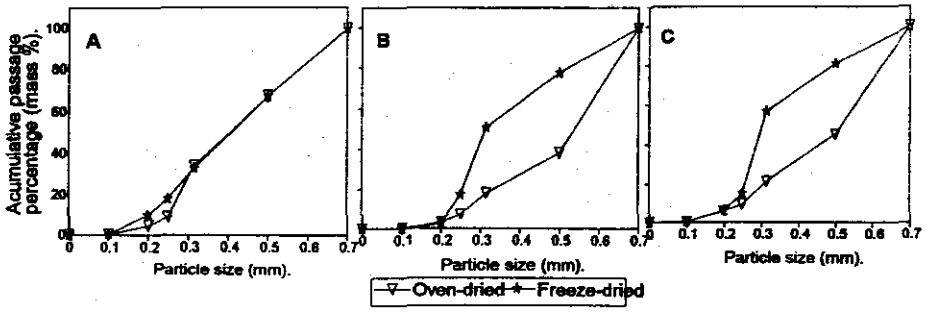

Fig. (2): Particle size distribution of buffalo's milk caseinate powders: (A) Total milk proteinate, (B) Lactic acid casein, (C) Rennet casein.

This means that the oven dried casein samples delivers particle groups which mainly lie in the coarse fraction, while freeze-dried samples delivers powders with finer fractions. However, the median values (X_{50}) of caseinate powders obtained in the present work were at least four-fold higher than those reported for high-fat milk powders (Keogh *et al.*, 2002). The modal value (X_h) gives the mean size of the particle fractions with the highest distribution density (q). In Table (3), these particular fractions were highlighted. As seen, the modal value of oven-dried lactic acid casein and rennet casein was 0.6 mm, while those of freeze dried sample was 0.283 mm, which reflect the remarkable differences in the distribution densities of oven dried and freeze dried casein powders. The specific surface area of the obtained casein powder, (mm^2/mm^3) ranged between 20.68 to 28.99, where the higher values belonging to the freeze-dried samples and the lower values belonging to oven-dried samples. According to Keogh *et al.*, (2002), the specific surface area of milk powders was decreased as the particle size of the powder was increased. Sauter diameter (d_{32}) gave values in the range of 0.207 to 0.290 mm, which were much lower than Xr, X_{50} values given in the present work. This means that the obtained particles of the caseinate powders were not exactly spherical in shape and consists mainly of broken spheres.

The fineness modulus of the oven dried caseinate samples was in the range of 3.8 to 4.286, while that of freeze-dried samples was in the range of 3.415 to 3.66. The fineness modulus is correlated directly with the average size of particle group and higher fineness modulus values will give higher average particle size (Hall, 1972). The uniformity index given in Table (4) show that the particle collectives of oven-dried samples lie in the coarse and medium particle groups, while the proportion of the fine group's increase in the freeze-dried casein samples. Fig. (2) gives the accumulative particle size distribution of the obtained casein powder. As seen, remarkable differences have been observed between the oven-dried and freeze-dried casein samples. Such distribution curves could be best represented mathematically by a logarithmic relationship developed by Rosin, Rammler, Sperling and Bennet (RRSB-distribution function) as follows (Stiess 1995):

$$\text{Ln (Ln 1/1-D)} = \text{Ln b} + \text{n Ln} \quad (10)$$

Where: D is the passage percent, x is the mean particle size between two successive sieves, b and n are constants. Sieve analysis data given in Table (3) were analyzed according to equation (10) using special logarithmic paper and the obtained constants were given also in Table (4). As seen, n- values for caseinate powders were relatively high and ranged between 2.9 to 3.45. According to Stiess (1995) n- values higher than 1 means that the tested powders contains low fraction of fine particle size and narrow distribution of the particle size in the tested powder. n- parameter given in Table (4) show that the particle groups of the oven -dried caseinate samples were coarser than those of the freeze-dried samples. The constant b in equation (10) is directly correlated with the so-called statistical particle mean size ($\bar{d}$) which could be obtained from the plotted curve at a passage percent of 63.67%. $\bar{d}$-values were also included in Table (4), which gives relatively higher values reaching between 0.41 to 0.53 mm and representing the higher coarsing of the obtained powders. The different mean values given in Table (4) stress the importance in expressing particle mean values of dairy and food powders, because of the diversity of the expressions used in giving the particle size values.

Bulk density:

The bulk density of the obtained casein powder was determined separately for each particle size group, and the results are presented in Fig. (3). As seen, bulk density of casein powders were increased by increasing particle size and the rate of increase was more remarkable for groups of particle size higher than 0.25 mm. Within the same group of particle size, oven-dried casein powders showed higher bulk density values than those obtained for freeze dried samples. Higher density values mean more compactibility of the individual particles, while lower bulk density values mean more porosity. Bulk density values obtained in the present work ranged between 0.35 to 0.7 g/cm^3. Furthermore, total milk proteinate and rennet casein powders (oven or freeze-dried) showed higher bulk density values than those of lactic acid caseins. The obtained result agree with those reported by Harish and Bhat (2004) and were higher than those reported for spray dried soymilk (Sanjeev *et al.*, 2003). However it was observed (Yetismeyen and Deveci 2000 as well as Gursoy et al., 2001) that storage period (6 months) increased the bulk density values of milk powders.

Effect of water activity on colour parameters of caseinate powders.

The tristimulus colour parameters, lightness (L), redness (a), yellowness (b), Hue angle (tan^{-1} b/a), chroma (C) and colour intensity (ΔE) were calculated for the caseinate powders immediately after drying and at the end of equilibrium time (30 days) at the different water activity values and the data are given in Table (5). As seen, colour parameters of the caseinate powders were affected by the applied preparation and drying methods. Freeze-dried samples were characterized by higher L and lower b values than oven dried samples. This could be refered to the effect of the temperature (60°C) in the oven-dried samples on the formation of browning component compared with the freeze dried samples.

Table (4): Particle size parameters of buffalo's milk caseinate powders.

Parameter	Value	Total milk proteinate		Lactic acid casein		Rennet casein	
		Oven dried	Freeze dried	Oven dried	Freeze dried	Oven dried	Freeze dried
Mean particle size standard deviation	Xr (mm) S±	0.412 ± 0.239	0.4057 ±0.235	0.4904 ±0.297	0.3744 ±0.2183	0.4750 ±0.2849	0.3593 ± 0.1599
Median value	X_{50}(mm)	0.40	0.405	0.540	0.310	0.53	0.31
Modal value	X_h(mm)	0.283	0.283	0.60	0.283	0.60	0.283
Specific surface area	Sv $(mm)^{-1}$	24.84	26.613	20.682	27.409	22.545	28.989
Sauter diameter	d_{32}(mm)	0.2415	0.225	0.290	0.2189	0.2661	0.2070
Fineness modulus	-	3.80	3.66	4.286	3.520	4.169	3.415
Uniformity index	-	3:6:1	3:5:2	6:3:1	2:6:2	5:4:1	2:6:2
n-parameter	-	3.15	2.45	3.45	4.0	2.9	3.3
Particle diameter at 63.7% passage	$\bar{d}$ (mm)	0.50	0.455	0.53	0.42	0.520	0.41

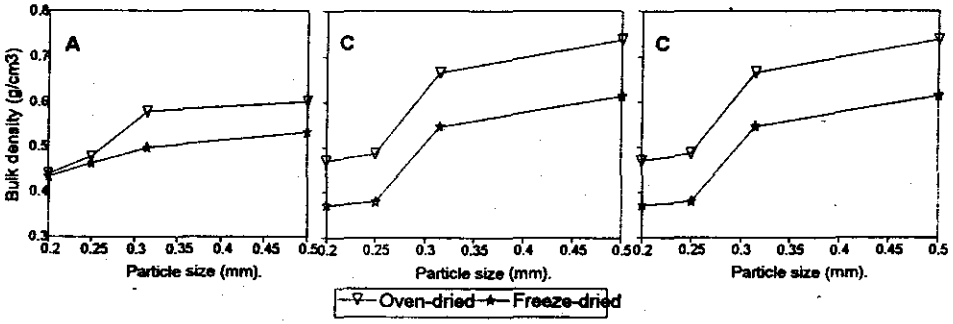

Fig.(3): Bulk density in relationship to particle size of buffalo's milk caseinate powder.
(A) Total milk proteinate (B) Lactic acid casein. (C) Rennet casein.

Lactic acid precipitated caseinate showed tendence to form a light- green colour note, since their a values were negative. Accordingly, chroma values of the oven-dried caseinate powders were higher than their corresponding freeze-dried samples. Chroma values of oven-dried samples ranged from 8.63 to 12.94, while those of freeze-dried samples were in the range of 6.87 to 8.209. The colour parameters of the caseinate powders were affected also by the surrounding relative humidity (water activity) during storage. As seen in Table (5), the lightness (L-values), were decreased, while redness (a-values) and yellowness (b-values) were increased during storage of caseinate powders at different water

Table (5): Colour parameters and total colour index of buffalo's milk caseinate powder at different water activity values .

Water activity	Oven- dried total milk proteinate						Freeze- dried total milk proteinate					
	Lightness L	Redness a	Yellowness B	Colour index ΔE ab	Hue angle	Chroma C	Lightness L	Redness a	Yellowness B	Colour index ΔE ab	Hueangle	Chroma C
Control	81.94	+0.977	9.07	82.44	+83.85	9.122	88.37	+2.20	6.51	88.63	+71.32	6.871
0.11	80. 71	+2.08	9.80	81.32	+77. 98	10.018	87. 56	+2.73	10.29	88.20	+75.11	10.645
0.22	79.55	+2.01	7.76	79.95	+75.47	8. 016	87. 30	+3.15	8.62	87.78	+69.93	9. 177
0.33	79.41	+2.10	21.71	82.35	+84.45	21. 811	85. 57	+1.29	17.61	87.37	+85.80	17.657
0.44	77.21	+3.26	18.70	79.50	+80.10	18.982	86.01	+1.68	16.53	87.60	+84.16	16.615
0.55	81.28	+1.98	16.13	82.88	+82.96	16.251	87.01	+6.19	15.35	88.57	+68.02	16.551
0.66	75.19	+4.55	34.34	82.78	+82.44	34.640	82.51	+1.45	30.14	87.85	+87.22	30.174
0.75	78.64	+2.25	17.83	80.66	+82.80	17.971	86.59	+1.76	17.13	88.28	+84.12	17.220
0.85	80.06	+3.42	17.18	81.95	+78.71	17.516	86.96	+2.31	13.11	87.97	+79.99	13.311
	Oven -dried Lactic acid casein						Freeze -dried Lactic acid casein					
Control	81.20	-2.460	12.30	82.16	-78.69	12.543	86.41	-0.874	8.07	86.79	-83.81	8.122
0.11	79.52	+0.663	13.40	80.64	+87.16	13.416	85. 47	+3.22	8.82	85.98	+69. 94	9.396
0.22	79.62	+0.923	12.79	80.64	+85.87	12. 823	85. 77	+2.96	7.63	86.15	+68.79	8. 190
0.33	76.85	+2.60	21.96	79.96	+83.24	21. 96	84. 31	+1.73	19.33	86.52	+84.88	19.40 9
0.44	76.17	+1.30	2.83	76.23	+65.32	3.114	83.96	+2.98	16.27	85.57	+79.62	16.541
0.55	78.34	+1.39	16.04	79.97	+85.04	16.100	84.48	+2.61	15.22	85.88	+80.26	15.446
0.66	82.51	+1.45	30.13	87.85	+87.24	30.164	80.02	+3.13	29.40	85.31	+83.92	29.573
0.75	77.88	+2.81	17.37	79.84	+80.81	17.595	83.36	+2.26	17.94	85.30	+82.81	18.086
0.85	79.14	+2.37	18.10	79.14	+82.54	18.254	85.55	+1.97	14.41	86.78	+82.21	14.548
	Oven -dried rennet casein						Freeze -dried rennet casein					
Control	85.61	+0.421	8.62	86.05	+87.20	8.630	87.48	+0.64	8.18	87.87	+85.46	8.209
0.11	85. 19	+1.66	10.07	85.80	+80.59	10.211	81. 91	+1.71	8.05	82.33	+78. 01	8.234
0.22	84.47	+2.14	10.09	85.10	+77.98	10.317	82. 95	+2.50	8.35	83.41	+73.33	8. 719
0.33	82.45	+2.22	21.37	85.21	+84.05	21.495	79. 10	+1.84	22.09	82.15	+85.23	22.176
0.44	84.16	+1.86	15.28	85. 56	+83.04	15.401	79.67	+1.87	12.50	80.66	+81.49	12.646
0.55	84.07	+1.79	16.37	86.37	+83.75	16.472	81.65	+1.69	15.29	83.09	+83.66	15.389
0.66	79.71	+4.69	27.92	84.59	+80.45	28.320	75.65	+3.69	32.59	82.45	+83.52	32.801
0.75	84.22	+1.57	15.41	85.64	+84.16	15.493	80.95	+2.43	18.37	83.04	+82.46	18.539
0.85	84.45	+0.976	14.64	86.70	+86.18	14.675	81.00	+0.62	12.75	82.06	+87.19	12.772

activity values (from 0.11 to 0.85). It was reported that the most drastic decrease in the lightness – values and the increase in yellowness-values of the caseinate powders were achieved at water activity values of a_w = 0.33 and a_w = 0.66-0.75. For example, the lightness values were decreased from an average of 82.9 and 87.42 to 77.03 and 82.99, respectively for oven-dried and freeze-dried caseinate samples stored at a_w _ value = 0.33. At water activity values a_w = 0.66-0.75, the lightness (L-values), were decreased, while redness (a-values) and yellowness (b-values) were increased during storage of caseinate powders at different water activity values (from 0.11 to 0.85).

Accordingly, the yellowness (b-values) of the caseinate samples has reached its maximum also at water activity values of 0.33 and 0.66 for all tested caseinate samples. The average (b) values of the oven – dried caseinate samples was 9.99 immediately after drying and reached 21.68 and 30.79 after 30 days of storage at water activity value of a_w = 0.33 and a_w = 0.66, respectively. The corresponding b-values of freeze-dried caseinate samples were 7.58, 19.67 and 30.71, respectively. As a result of decreasing lightness and increasing yellowness, the chroma value was also increased (Table, 5). The drastic increase in yellowness and chroma values of the tested caseinate powders at a_w = 0.33 and a_w = 0.66 may be explained by the change in the three phases of the sorption isotherm curves given in Fig (1). As seen, water activity value of a_w = 0.33 was representing the end of phase one (increase moisture content), while a_w = 0.66 or 0.77 was the end of phase two and start of phase three. The obtained results revieled that the change in colour of caseinate powders was acceptable at water activity values up to 0.55, except at a_w = 0.33. The change in colour from cream colour to pale brown during storage of milk powders was reported also by Ford *et al.*, (1983) and Burin *et al.*, (2001), which could be referred to the deterioration by Millard browning reaction. On the other side, the results obtained in the present work agree with those reported by Ramirez-Jimenez *et al.*, (2004), where they stated that infant cereals containing powdered milk developed yellow colour during storage at a wide range of water activity values.

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بعض الخواص الفيزيائية لكازينات اللبن الجاموسى المجففة

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يهدف هذا البحث إلى دراسة بعض الخواص الفيزيائية لكازينات اللبن الجاموسي والتي تم تحضيرها تحت ظروف مختلفة من الترسيب ثم تجفيفها في فرن على درجة حرارة ٦٠°م وكذلك باستخدام طريقة التجفيد. تم طحن العينات المجففة باستخدام مطحنة شاكوشية ثم تم دراسة كل من: المحتوى الرطوبي الاتزانى لها على درجات نشاط مائي مابين ٠,١١ الى ٠,٨٥ ودرجة حرارة ٣٠°م وخواص التوزيع الحجمى للحبيبات بواسطة استخدام مجموعة المناخل القياسية و تقدير الكثافةالسائبة و خصائص اللون مثل معامل السطعان (L) و الاحمرار(a) والاصفرار(b). وكذلك شدة اللون للعينات المحضرة.

أثبتت النتائج أن محتويات الرطوبة الاتزانية لعينات الكازين المجففة كانت أعلى من مثيلاتها المحضرة بالتجفيف على ٦٠°م عند تركها للاتزان تحت ظروف مختلفة من درجات النشاط المائي تراوحت من ٠,١١ الى ٠,٨٥ وقد بلغت قيمة الرطوبة الدنيا لطبقة جزيئات الماء الأحادية اللازمة لتغطية أسطح البروتين بطبقة واحدة من الرطوبة مابين ٠,٠١٣ الى ٠,٠٥٩٣ جم ماء لكل جم مادة جافة بينما بلغت قيم معامل الطاقة الحرارية مابين ١٥,٥٥ الى ١٠٣,٩٦ لعينات الكازين المجففة على ٦٠°م، ١٥,٤٤ الى ٢٣,٤٩ لعينات الكازين المجفدة مما يدل على مدى شدة ارتباط جزيئات الماء بالكازينات المجففة على٦٠°م ومدى انضغاطية جزيئات الكازينات المجففة على ٦٠°م. ولقد تراوح متوسط حجم الجزيئات في مساحيق الكازين مابين ٠,٤٩٠٤ مم للكازينات المحضرة بحمض اللاكتيك و المجففة على٦٠°م الى ٠,٣٥٣٩ لعينات الكازين المحضرة بالمنفحة والمجفدة. كما تم أيضا حساب كل من متوسطات المنوال والمتوسطات المودالية وكذلك المساحة السطحية النوعية ومعاملات النعومة لمساحيق الكازين المحضرة.

ولقد أكدت النتائج زيادة قيمة الكثافة السائبة للمساحيق بزيادة حجم الجزيئات وكان معدل الزيادة واضحا عند كبر قطر جزيئات المساحيق عن ٠,٢٥ مم ولقد أوضح كل من مسحوق بر وتينات اللبن الكلية وكازينات المنفحة سواء المجففة على٦٠°م أو المجفدة قيما أعلى للكثافة السائبة عن مثيلاتها المحضرة باستخدام حمض اللاكتيك. كما وجد أن معاملات اللون لمساحيق الكازين تتأثر بكل من طريقة التحضير والتجفيف حيث تميزت مساحيق الكازين المحضرة بالتجفيد بأنها كانت أكثر سطاعة وأقل إصفرارا من مساحيق الكازين المجففة على٦٠°م. كما وجد أن قيم السطعان تنخفض بينما تزداد كل من قيم الاحمرار والاصفرار أثناء تخزين مساحيق الكازين على قيم درجات نشاط مائي مختلفة تراوحت من ٠,١١ إلي ٠,٨٥.